

Cold molecules produced by intense optical pulses

Understanding the detailed dynamics that molecules and atoms experience while colliding with one another is important in understanding the fundamentals of chemistry. Sandia researchers are investigating various techniques to slow molecules down in order to produce samples of ultra-cold molecules. By monitoring their interactions in a slow-motion environment, CRF scientists can observe their behavior more precisely.

When molecules move slowly at a few centimeters per second with respect to each other they are said to be ultra-cold. An ultra-cold molecule has so little momentum that its de Broglie wavelength becomes the same order of magnitude as its size, allowing one to observe its wave nature. CRF researchers are developing new experimental techniques to produce molecules in this low-temperature regime (typically below tens of millikelvin). Once produced, researchers will then study their interactions. These tools will enable the measurement and control of collision dynamics with increased fidelity. One technique that scientists are investigating to slow molecules is described here.

Recently, Sandia researcher Dave Chandler, and postdocs Jaime Ramirez-Serrano and Kevin Strecker succeeded in slowing down H_2 molecules that were initially moving at supersonic speeds after expansion from a high-pressure nozzle. They achieved this by using a focused laser beam that was not resonant with any transition in the H_2 molecule.

This technique is applicable to a wide range of molecular species, as it exploits the force that molecules experience when

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Examining the chemistry of isomers

Understanding the chemistry of isomeric species is integral to unraveling major technical challenges in combustion science such as pollutant generation (soot in particular) and ignition control. The CRF is addressing these challenges with a new, uniquely powerful kinetics reactor that uses synchrotron photoionization mass spectrometry. This photoionization approach to isomer-resolved detection has proved very successful in studies of flame chemistry, resulting in the recent identification of enols in a wide variety of flames. (C. Taatjes et. al, *Science*, Vol 308, 24 June, 2005, pp. 887-890 see *CRF News*).

One specific problem in which isomers may play determining roles in combustion chemistry is the formation of polycyclic aromatic hydrocarbons (PAHs) and soot, which impact both environmental and public health. A better understanding of their genesis could lead to new technologies that control soot formation. Interest has recently focused on the chemical pathways involved in forming the first benzene ring or similar aromatic molecules in flames. Such molecules are widely regarded as precursors to soot formation. To unravel this chemistry, scientists need techniques that can distinguish between structural isomers of molecules.

A new experimental apparatus constructed by a team of CRF scientists and colleagues at the Lawrence Berkeley National Laboratory (LBNL)

will address these problems with a new capability for isomer-resolved kinetics measurements of elementary reactions.

The experiment operates at the Chemical Dynamics Beamline of the Advanced Light Source (ALS) at LBNL. The team is led by David Osborn and Craig Taatjes of the Combustion Chemistry Department at the CRF in collaboration with Musa Ahmed and Steve Leone of

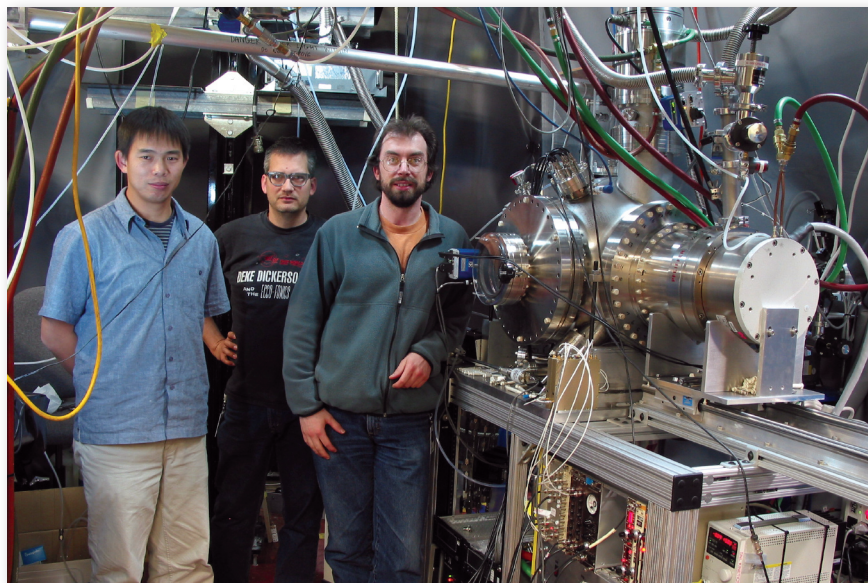


Figure 1. (From left to right) Post-doctoral scientist Peng Zou, Craig Taatjes, and David Osborn in front of the Multiplexed Chemical Kinetics Photoionization Mass Spectrometer at the Chemical Dynamics Beamline of the Advanced Light Source.

LBNL. Complementing the low-pressure flame apparatus at the ALS, which probes the complex web of reactions present in a flame, this new experiment isolates individual chemical reactions or sequences of reactions for more detailed study.

One of the most important reactions involved in forming the first aromatic rings is the $C_3H_3 + C_3H_3$ reaction, which has been the focus of several theoretical studies by Sandian Jim Miller and Stephen Klippenstein of Argonne National Labo-

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ratory. In this reaction, many isomeric forms of C_6H_6 are energetically feasible (e.g., benzene, fulvene, 1,2-dimethylenecyclobutene, etc.) and the energy landscape that connects them has been explored theoretically. It is important to know which isomers are produced in each chemical reaction step because some isomers are much more reactive than others.

The new apparatus constructed by the CRF/LBNL team is known as the Multiplexed Chemical Kinetics Photoionization Mass Spectrometer (Figure 1). It combines two powerful concepts that make isomer-resolved kinetics measurements possible. First, neutral molecules involved in the reaction are photoionized using the widely tunable (6–24 eV) vacuum ultraviolet (VUV) radiation from the ALS. Because different isomers usually have different ionization energies, each isomer can be identified by its unique photoionization efficiency threshold and shape. The continuous tunability of the ALS, with resolution of 10–30 meV, allows the scientists to select optimal ionization energy to detect each isomer. For example, the ability to distinguish allene from propyne (C_3H_4 isomers) and vinyl alcohol from acetaldehyde (C_2H_4O isomers) has recently been demonstrated in the ALS low-pressure flame chamber.

The second unusual feature of this experiment is the mass spectrometer. The design uses a small magnetic-sector instrument coupled to a time- and position-sensitive single-ion counting detector. This approach combines a mass spectrometer with a 100% duty cycle (like a quadrupole mass spectrometer) with the multiplex advantage of measuring a broad range of masses simultaneously (as in time-of-flight mass spectrometry). This detector also measures the time profile of each mass to provide kinetic information on the reaction.

Chemical reactions occur in a low-pressure (3–10 Torr) flow tube with a 400- μ m orifice for sampling the gas flow. A pulsed photolysis laser fires down the bore of the flow tube, creating a uniform distribution of radicals and initiating the reaction. Concentrations of all species are monitored by recording time-resolved mass spectra. As a first experiment, the scientists chose the simple oxidation reaction $CH_3 + O_2$ as a benchmark for the apparatus. Mass spectra as a function of time for this reaction are shown in Figure 2. In this system,

both methyl (CH_3) and acetyl (CH_3CO) radicals are generated from the photodissociation of acetone (CH_3COCH_3). As the chemical reactions begin, the decay of methyl radical reactants (CH_3) and the rise of methylperoxy products (CH_3O_2) can be easily identified. Temporal resolution is critical in assigning each species as a photo-dissociation, primary reaction, or secondary reaction product.

The multiple mass-detection capability of this apparatus is highly advantageous compared to traditional experiments that observe one mass at a time using quadrupole mass spectrometers. For example, Figure 2 shows simultaneously acquired time profiles of all masses from 10–75 amu. A weak, time-resolved signal is observed at mass 72, tentatively identified as $CH_3COC_2H_5$ arising from side reactions. Simultaneously observing a broad range of masses minimizes the possibility that certain reaction products, especially unexpected ones, will be ignored. Furthermore, mass multiplexing makes it easier to follow complex secondary chemistry from a series of reactions.

Although optimization of the apparatus will continue (the experiment has had only two runs at the ALS), the instrument has already produced new scientific results on the nature of alkylperoxy radicals (RO_2) and their cations. Alkylperoxy radicals are important intermediates in

autoignition and in the low-temperature combustion chemistry that is critical in emerging engine technologies, such as homogeneous charge compression ignition. Until the work of the CRF-led team, only the simplest alkylperoxy radical (CH_3O_2) had been detected using photoionization mass spectrometry, and its ionization energy was unknown. The new results include the first photoionization efficiency curves for CH_3O_2 , $C_2H_5O_2$, and $C_3H_7O_2$. While the methylperoxy cation is a stable species, the larger cations appear to be unbound with respect to dissociation to $R^+ + O_2$.

In addition to addressing problems in combustion chemistry, the capabilities of this new apparatus will be valuable in atmospheric, interstellar, and aerosol chemistry. The CRF/LBNL team is actively developing collaborations with external users. Such collaboration will broaden the impact of this instrument. Experiments have already begun in collaboration with Prof. Vadim Knyazev of the Catholic University and Prof. Simon North of Texas A&M University.

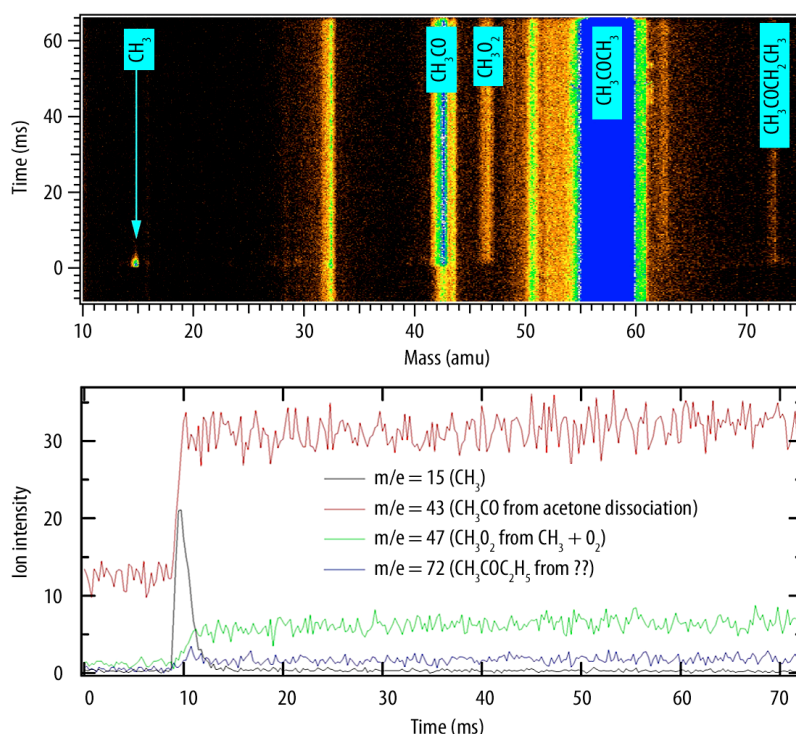


Figure 2. Time-resolved mass spectra of the $CH_3 + O_2$ reaction system at a photoionization energy of 10.2 eV. (false color)

50th Anniversary Celebration and Rededication

Sandia National Laboratories, California, is celebrating its 50th Anniversary.

Sandia employees, their guests, retirees, and VIPs will mark the occasion with three days of celebration and rededication activities.

On Tuesday, March 7, the celebration begins with round-table discussions with current and retired Sandians, ending with a seminar by author Richard Rhodes titled, "The History of Nuclear Deterrence."

On Wednesday, March 8, a plaque unveiling will kick off the ceremony. Keynote speaker, former Lawrence Livermore National Laboratory Director Dr. Johnny Foster will be joined by guests from the Department of Energy Office of Science, National Nuclear Security Administration, Department of Homeland Security and the national laboratories. VIP guests will also be on site Wednesday to tour the laboratories.

On Thursday, March 9, Linda Cohen, professor of economics at UC, Irvine; Susan Hackwood, executive director of the California Council on Science and Technology; and Maxine Savitz, director of The Washington Advisory Group will discuss "Science, Technology and Policy: The California Connection." Sandians are encouraged to invite adult family members and friends to tour the site. (Note: parking in the CRF lot will be diverted between February 23 and March 17). View the schedule of events and register guests by February 24 at <http://www.ca.sandia.gov/anniversary/index.php>

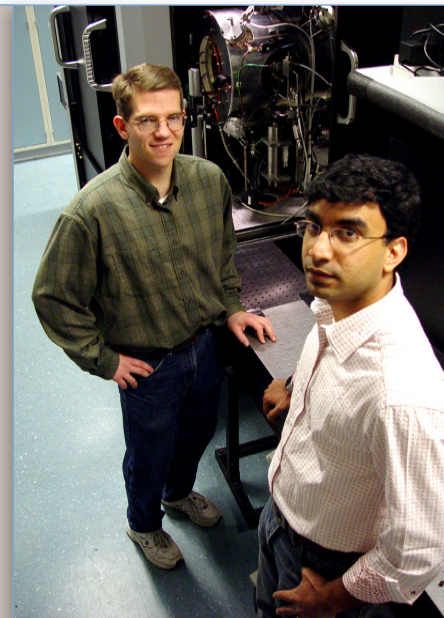


Paul Miles

Sandians garner multiple SAE awards

Paul Miles was elected a Fellow of the Society of Automotive Engineers (SAE). He has been with the engines group at Sandia for 13 years. SAE Fellowship status is the highest grade of membership bestowed by SAE. It recognizes outstanding engineering and scientific accomplishments by an individual that have resulted in meaningful advances in automotive, aerospace, and commercial vehicle technology. The program recognizes an average of only 20 worldwide recipients each year.

Cherian Idicheria won an oral presentation award for his paper titled "Soot Formation in Diesel Combustion Under High-EGR Conditions" and Lyle Pickett won an oral presentation award for the paper "Relationship Between Ignition Processes and the Lift-Off Length of Diesel Fuel Jets" at the SAE Powertrain & Fluid Systems Conference & Exhibition, October 2005 in San Antonio, TX. Idicheria and Pickett are in the Engines Group at Sandia and are working on clean, low-temperature diesel combustion. Pickett has been with Sandia for five years and Idicheria has been a post doctorate for one year. Sandian Pete Witze, now retired, won an award for his paper, "Comparison of Single- and Dual-Spray Fuel Injectors During Cold Start of a PFI Spark Ignition Engine Using Visualization of Liquid Fuel Films and Pool Fires" at the conference, his 5th SAE Excellence in Oral Presentation award.



Lyle Pickett (left) and Cherian Idicheria (right).

Mueller visits Caterpillar



Chuck Mueller has returned from a 3-month visit to the Caterpillar Technical Center in Mossville, Illinois, where he worked with the Advanced Combustion Team managed by Kevin Duffy. Mueller's activities focused on developing low-temperature combustion strategies to meet stringent emissions regulations that come into force in 2010 and 2014 for on-and off-highway engines, respectively.

Pictured from left to right are: Bill Hardy, Tony Rodman, George Donaldson (Level 2 manager), Jamie Smith, Parag Mehresh, Carl Hergart, Andy Kieser, Mike Liechty, Bill Moser, Chuck Mueller, Andrew Gross, and Kevin Duffy.

Cold molecules (Continued from page 1)

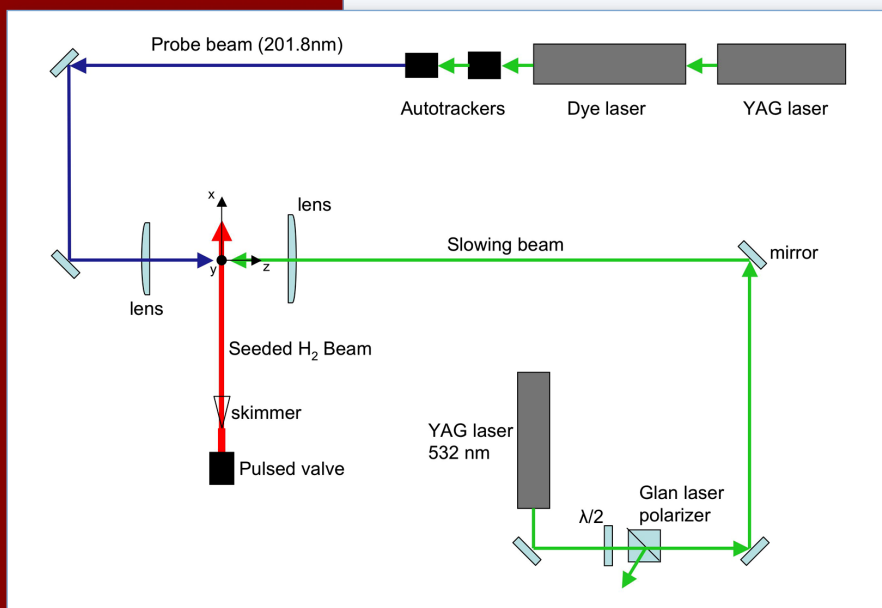


Figure 1. Experimental setup to slow down molecules in a molecular beam by using a single laser beam to create an optical Stark effect.

optical field. The force acts through the polarizability of the electron cloud of the molecule. As all atoms and molecules are polarizable to some extent, this appears to be a very general method for slowing molecules. Molecules experience a second-order Stark shift of their energy levels within high-intensity optical fields. This energy shift, while in the optical field of the molecule, slows the molecule. As the molecules decelerate, they are said to be colder. These strong optical-field gradients exist when focusing intense laser pulses such as the ones obtained by Nd:YAG pulsed lasers. The current experiments at the CRF use the 532-nm light from a Nd:YAG laser focused to produce laser intensities up to $1.59 \times 10^{12} \text{ W/cm}^2$.


Chandler's group measured the velocity distribution of the slowed molecules using the velocity-mapped ion-imaging technique developed in his laboratory. This technique produces an image of molecules after they have been laser-ionized. The velocity of the neutral molecules can be derived from this image. The slowed molecules show a velocity distribution that is dependent on the laser's intensity, with a velocity reduction as high as 24% when compared to the original velocity ($\sim 560 \text{ m/s}$) of the molecules in the supersonic beam.

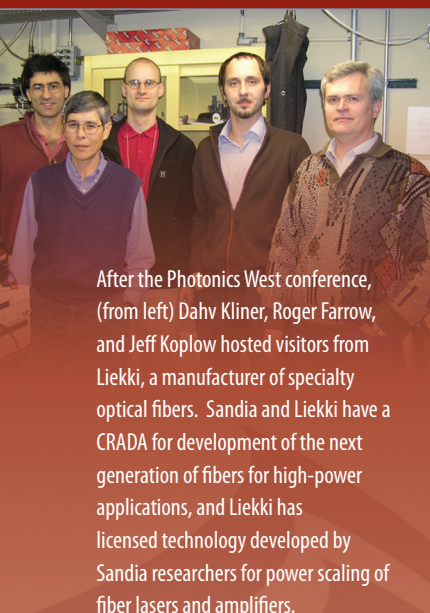
Figure 1 shows the experimental setup to produce and detect the slowed H_2 molecules with a single laser beam. (In the two-beam technique, the incoming single laser pulse is divided in two and then recombined at the interaction volume with the molecular beam, thereby forming an interference pattern to produce stronger optical gradients.) After a supersonic beam of H_2 molecules seeded in Argon is produced by opening a piezo-electric valve, two short 10-ns laser pulses are fired. The first one is the intense, off-resonant, 532-nm light that produces the slowing of molecules

by a second order optical Stark effect. The second pulse is a probe laser with a wavelength of 201.8-nm that ionizes the H_2 molecules, allowing them to be detected by the ion-imaging apparatus. The velocity distribution of the H_2 molecules in the beam is determined by analyzing the image after the appropriate background subtraction has been performed. The researchers adjusted the timing and position of the probe laser beam to probe the velocity distribution of only the molecules affected by the first laser shot.

Figure 2 shows the velocity distributions as a function of 532-nm laser power. As laser power is increased, the speed of the molecules within the focus of the laser beam either increases or decreases, depending upon their initial position. Molecules that move toward higher laser intensity while the 9-ns laser pulse is present will speed up, while molecules that were initially at the center of the laser focus and are now moving toward lower laser intensity will slowdown. The highest laser intensity of $1.59 \times 10^{12} \text{ W/cm}^2$ corresponds to a case when all the power of the 9-ns long, 532-nm laser pulse of approximately 500 mJ of laser light is focused to a spot size of $50.3 \times 10^{-6} \text{ cm}^2$.

The lower image shows the original velocity distribution of the atoms in the molecular beam traveling at a mean velocity of 560 m/s^{-1} . The upper six images are the resulting velocity distribution of the H_2 molecules after interacting with the intense Nd:YAG laser.

Besides these investigations utilizing laser light to slow down molecules, Chandler's group is also concentrating on producing cold molecules by a kinematic cooling technique that relies upon molecules colliding with atoms of a particular mass in order to cool them. Once produced, cold molecules will form an interesting tool to study chemical dynamics and the details of the potential curves that control the interaction of molecules as they react. 



After the Photonics West conference, (from left) Dahv Kliner, Roger Farrow, and Jeff Koplow hosted visitors from Liekki, a manufacturer of specialty optical fibers. Sandia and Liekki have a CRADA for development of the next generation of fibers for high-power applications, and Liekki has licensed technology developed by Sandia researchers for power scaling of fiber lasers and amplifiers.

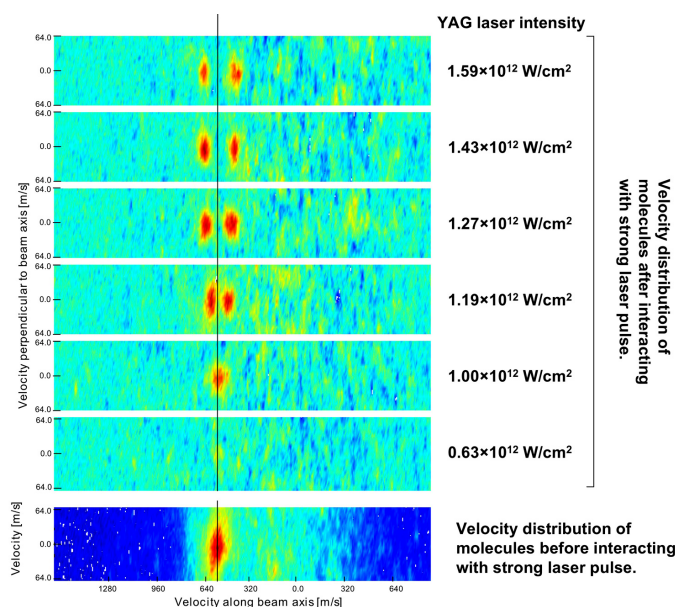


Figure 2. Velocity distribution of H_2 molecules before and after interacting with an intense optical field produced by a 532-nm pulsed laser.

Terascale direct simulations reveal intricate coupling between turbulent mixing and finite-rate chemistry in turbulent CO/H₂ slot jet flames

Certain engine types, such as those that power jet aircraft, as well as direct injection diesel and gasoline engines operate under conditions of turbulent combustion in which streams of fuel and air are injected separately. Achieving the optimal balance of fuel to air molecules is crucial for the chemical reactions of combustion to occur. The right amount of turbu-

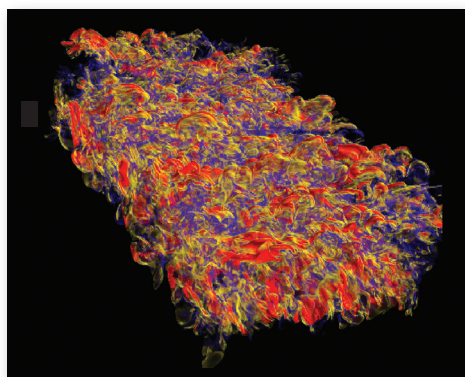


Figure 1. A simulated planar jet flame, colored by the rate of molecular mixing (scalar dissipation rate), which is critical for determining the interaction between reaction and diffusion in a flame. The image shows that high scalar dissipation regions exist in thin, highly intermittent structures aligned with principal strain directions. (Visualization created using a volume rendering application written by Hongfeng Yu and Kwan-Liu Ma, UC Davis.)

lence improves the efficiency of combustion by increasing the rate of mixing and hence heat release. However, too much turbulence interrupts the chemical reaction, partially extinguishing the flame. Areas of unburned fuel–air mixture that fail to reignite promptly may increase exhaust emissions and reduce fuel efficiency. If pervasive enough, the flame can destabilize or completely blow out.

To better understand the intricate relationship of turbulence, turbulent mixing and finite-rate chemical reactions, CRF researchers Jacqueline Chen, Evatt Hawkes, and Ramanan Sankaran of Sandia National Laboratories conducted the largest direct numerical simulation of its kind ever done. Using a computer allocation from a 2005 DOE Innovative and Novel Computational Impact on Theory and Experiment (INCITE) award, the researchers performed the first three-dimensional direct numerical simulations (DNS) of a turbulent nonpremixed H₂/CO–air flame with detailed chem-

istry (Figure 1) at National Energy Research Scientific Computing Center at Lawrence Berkeley National Laboratory (NERSC). Also, at the Molecular Science Computing Facility/Pacific Northwest National Laboratory and as ‘early’ users of the Leadership Class Supercomputers at Oak Ridge National Laboratories, the CrayX1E and CrayXT3, they made additional simulations with up to half a billion grid points as part of a parametric study in Reynolds number *Re* (the ratio of the inertial to viscous forces).

Small-scale turbulence–chemistry interactions such as extinction and reignition, flow and flame unsteadiness as well as differential diffusion of chemical species, are difficult to measure experimentally. Canonical simulations, which resolve all of the temporal and spatial scales of the flow and scalars, can provide structural and statistical information associated with the scalar dissipation rate field, i.e. the dissipation of fluctuations of mixture fraction and reactive scalars in a turbulent flow. To simulate combustion in practical systems, engineers use a spatial grid that is too coarse to capture these small-scale phenomena. Mathematical models can approximate the microphysics of combustion. These models are often empirical and are not predictive. But innovations in supercomputers now enable researchers to directly tackle questions about turbulence–chemistry interactions. Statistics obtained from these calculations can be used to validate and improve models.

The initial data analysis shows for the first time how detailed transport and finite-rate chemistry effects can influence the mixing of passive and reactive scalars.

Molecular mixing is the central modeling issue in a key combustion model, the transported probability density function (pdf) approach. In this framework, the mixing timescale and resulting model predictions depend

upon the choice of the timescale. Nominally, the timescale is assumed to be the same for all scalars, and the same order of magnitude as the large scale turbulence timescale. But in flames, differential diffusion between species and the strong interplay between mixing and reaction may degrade these assumptions. It is difficult to directly assess these assumptions in a-posteriori tests, and measuring reactive scalar mixing is not yet possible for all species. DNS of reacting flows with detailed chemistry can evaluate these assumptions.

The DNS data show that the turbulence-to-scalar mixing timescale ratio for a conserved scalar (mixture fraction) is close to unity and nearly independent of Reynolds number at sufficiently high Reynolds numbers. On the other hand, differences in species molecular diffusivities and finite-rate chemical effects were found to affect this timescale ratio for reactive species by as much as a factor of three. For major species, there is a decline in the dependence of this timescale ratio on molecular diffusivity with increasing Reynolds number, though a weak depen-

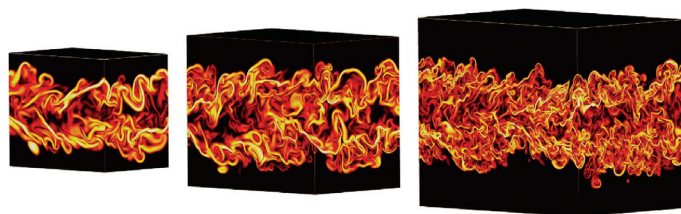


Figure 2. Instantaneous isocontours of the total scalar dissipation rate field for successively higher Reynolds numbers (from left to right) at a time when re-ignition following extinction in the domain is significant. The dissipation fields are organized into thin sheet-like lamellar structures, with lengths far exceeding their thickness, consistent with experimental observations in nonreactive flows. Increasingly fine-scaled structures are observed at higher Reynolds numbers. (From E. R. Hawkes, R. Sankaran, J. C. Sutherland, and J. H. Chen, “Direct Numerical Simulation of Temporally-Evolving Plane Jet Flames with Detailed CO/H₂ Kinetics,” submitted to the 31st International Symposium on Combustion, 2006.)

dence exists at the highest Reynolds number simulated, *Re*=9000. Chemical reaction effects on reactive scalar mixing were noted for minor species, however, and persist to high Reynolds numbers as they involve strong interaction between chemistry and diffusion. The mixing attributes of these species depends not only on their local turbulence production and dissipation balance, but also on reaction.

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Terascale direct simulations

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To ramp up to the large INCITE calculations and those performed at the National Center for Computational Sciences/Oak Ridge National Laboratory, Chen's team ported and optimized their DNS code, S3D. With the help of NERSC and ORNL staff, the code runs twice as fast on the IBM SP3 at NERSC and ten times faster on the CrayX1E at ORNL.

This fine-tuning helped the researchers achieve the highest-ever Reynolds number in a 3D fully resolved DNS of a nonpremixed flame with detailed chemistry. Simulating different Reynolds numbers illuminated "intermittency"—the intense, localized fluctuations in a turbulent flow. Such fluctuations can cause localized extinctions and reignition in the combustion process. The results show the link between scalar intermittency and the Reynolds number (Figure 2). As the Reynolds number, and hence, scalar intermittency increases, a greater degree of local extinction is observed and it takes longer to reignite the extinguished regions. Varying degrees of extinction for the three cases are demonstrated by the conditional pdf of the mass fraction of the OH radical and its conditional Favre mean (see Figure

3). Note that the pdf remains monomodal for the CO/H₂ mixture, consistent also with earlier experimental observations. The DNS data show that the high intermittency is manifested by a near lognormally distributed scalar dissipation rate conditional on the stoichiometric mixture fraction.

The INCITE and NCCS/ORNL projects generated 30 TB of raw DNS data, which is being analyzed to understand the turbulent mixing of reactive scalars and extinction and reignition dynamics. The data will eventually be shared with the combustion modeling community. To assist with the daunting task of gleaning physical insight from terascale simulated data, Chen's group is working closely with computer scientist Kwan-Liu Ma of the University of California at Davis to develop feature extraction tools and interactive multi-variate visualization capabilities for spatial and time-varying data. These capabilities will help researchers understand how turbulent mixing interacts with chemical reactions. Scientists are also working to understand phenomena including the dynamic behavior at flame edges and cusps, the formation of extinction pockets, and the mechanism by which these pockets reignite.

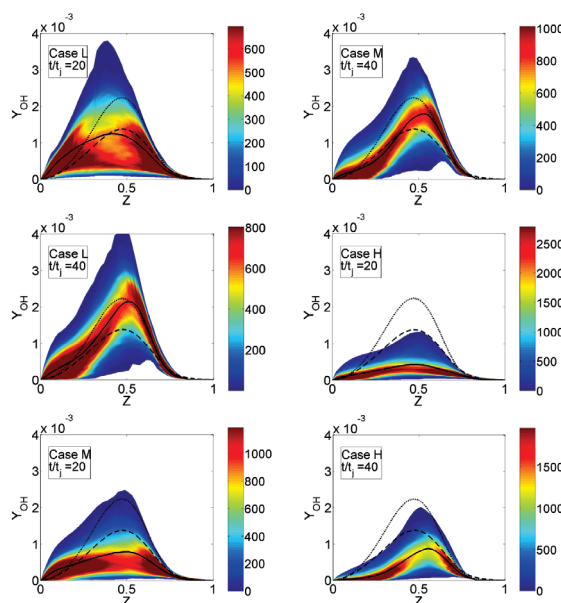


Figure 3. Conditional probability density functions (color scales), conditional means (solid line), initial values (dotted lines) and a steady laminar flamelet value near extinction (dashed line) of OH mass fraction for successively higher Reynolds numbers (case L Re= 2500, case M Re= 4500, case H Re= 9000) at 20 (maximum extinction in domain) and 40 (reignition in domain) jet times.

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